



Full Length Article

Catalytic activity of calcined scallop shell for rapeseed oil transesterification to produce biodiesel



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ABSTRACT

Catalytic activity of the calcined scallop shell for rapeseed oil transesterification to produce biodiesel was examined as compared to the calcined limestone, with focusing on Na content of the source material. While an appreciable amount of Na was detected for scallop shell (0.33%), limestone was near Na free (less than 0.01%). For the salty limestone prepared by immersing in a NaCl aqueous solution for two weeks, the Na content was 0.30%. The scallop shell and the salty limestone were calcined into much less active catalyst than the original limestone. Also, the less active catalysts from the salty sources were formed out of larger crystallite of lime phase and displayed the weak basicity. On the other hand, the crystalline size of lime phase became smaller by blending the shell source with basic-MgCO₃ prior to the calcination. The blending modification markedly enhanced the catalytic activity of the calcined scallop shell.

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1. Introduction

Plant oil is one of the biomass resources that are useful in resolving globally environmental problems such as greenhouse gas emission and depleting fossil fuel, and is commonly utilized as a source for alternative petroleum diesel fuel consisting of fatty acids methyl ester (FAME). For the existent process to produce the alternative petroleum diesel fuel, which is termed as “Biodiesel”, plant oil is transesterified with methanol with the help of homogeneous base catalysis of alkali hydroxide [1]. The homogeneous base catalyst has advantage of the fast reaction rate but causes serious alkalization of the by-produced glycerol and an oily wastewater [2]. These waste effluents give rise to not only the costly production but also a decline in sustainability of biodiesel utilization.

For the purpose of resolving the problems mentioned above, many researchers have been studying the heterogeneous base catalyst, such as the calcined hydrotalcite [3,4], supported alkali catalyst [5,6], anion-exchange resin [7,8] and organic base grafted over metal oxides and so on [9,10]. Among these candidates, calcium oxide (CaO) is superior in not only the catalytic activity but also the cost effectiveness [11,12]. The highly activated CaO could be prepared by calcining the industrial carbonate source such as limestone under the moisture-CO₂ free condition, and 1 wt% of

the catalyst loading brought about 90% of the FAME yield within 1 h at reflux of methanol [13]. Although the CaO catalyst was transformed into calcium diglyceroxide by reacting with the by-produced glycerol [14], the transformed matter could be reused for the transesterification without deactivating appreciably [15]. For an issue of partial leaching of the CaO catalyst, which deteriorates its stability and fouls the produced biodiesel, the some resolving technologies have been studied successfully [16–18]. Also, there are some interesting research works to modify the CaO catalyst: preparation of porous CaO with the aim of enhancing catalytic activity [19], combination with photo-catalyst in order to achieve the sustainable production [20], and so on.

On the other hand, much interest is taken in various seashells as a source material of the CaO catalyst with a view to recycling waste material [21–27]. Many of shellfish farms seem to be racked with stink from a large amount of the shell waste. Therefore, the recycle of shell leads to solution of the environmental problem mentioned above, as well as economical production of biodiesel. These improvements are surely useful in enhancing the sustainability of biodiesel utilization. For most of the concerning research works, above 5 wt% of the catalyst loading was required for achieving the reasonable reaction rate. Since the required loading amount was larger for the shell-based catalyst than for the calcined pure carbonate [11], it seems that the shell-based catalyst seems to be less active in the plant oil transesterification. However, there is few research works where the transesterifying activity of the shell-based catalyst was investigated in detail.

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For a present research work, the scallop shell that is one of the typical wastes from Japanese shellfish farm was employed as a source material of the CaO catalyst. The catalytic activity of the calcined scallop shell for rapeseed oil transesterification was evaluated as compared to the calcined limestone. Since shellfish inhabits in seawater and necessitates NaCl for the life activity, it is certain that NaCl is contained in a variety of seashell. Indeed, there is a research paper indicating that Na was detected as the elemental impurity of seashell [23]. On the other hand, it is reasonable from the geo-chemical viewpoint that limestone does not contain NaCl at all. Therefore, a difference in the catalytic activity between the calcined scallop shell and the calcined limestone was discussed with focusing on Na content of the source materials for this work. Also, the salty limestone was prepared by immersing in a NaCl aqueous solution, for imitating the shell source. The prepared catalysts were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Infra-red (IR) spectroscopy, for the purpose of deepening the discussion about the catalytic activity. The basicity was measured by using Hammett indicators. Following the evaluation of the catalytic activity, modification of the shell-based catalyst by blending the shell source with basic-MgCO₃ prior to the calcination was studied. The CaCO₃-MgCO₃ binary mineral, termed as “Dolomite”, could be calcined into the highly-activated catalyst, in comparison to limestone [26].

2. Experimental

2.1. Catalyst preparation

Scallop shell was offered from a local market. After rinsing with distilled water for eliminating the solid impurities, the scallop shell was dried at 373 K for 12 h in an oven. Then, the scallop shell was ground by a cutter mill of desktop type. The product powder, which passed through a sieve of 100 μm mesh, was employed as a source material of the CaO catalyst. The powdery limestone was purchased from a domestic mining site (Ni-imi Chemical Co. Ltd.). The average particle diameter was 1.2 μm. Also, the limestone source was salted by immersing it in NaCl aqueous solution for two week, in order to prepare an imitation of the shell source. NaCl content of the immersing solution (3.5%) was determined with referring to seawater. Additionally, the reference catalysts to elucidate the influence of the impurity were prepared by adding SiO₂ and Al₂O₃ fine particles to the limestone source in a mortar. The SiO₂ and Al₂O₃ additives were purchased from Wako chemicals.

A variety of the source materials were calcined at 1173 K in an argon gas flow with a tubular furnace. Immediately after the calcination, the prepared CaO catalyst was subjected to the experimental transesterification and the instrumental characterization.

2.2. Instrumental characterization

For the prepared CaO catalyst, XRD pattern was measured on a Bruker D8 Advance using CuKα radiation, over a 2θ range from 10 to 50°. The completed calcination was validated from the diffraction pattern, and crystalline size of lime phase was determined from half of width for a (200) diffraction peak on the basis of the Scherrer equation. Also, a scanning electron microprobe (SEM) Hitachi S-4100 was operated at 3.0 kV of an accelerating voltage with 1 μA of an emission current, for discussing particle morphology of the CaO catalyst. Furthermore, Infra-red (IR) spectrum was recorded on a Parkin-Elmer Spectrum One analyzer operated with Attenuated Total Reflection (ATR) mode, for examining the surface hydroxylation and carbonation of the catalyst. Basicity of the

catalyst was measured by immersing it into toluene solution of Hammett-indicators: phenolphthalein, 2,4-dinitroaniline and 4-nitroaniline.

Additionally, source materials of the catalyst were characterized on an atomic absorption photospectrometer Shimadzu AA6300, a X-ray fluorescence (XRF) spectrometer Rigaku RIX-3000, and a thermo-gravimetric (TG) analyzer Mettler-Toledo TGA/DSC1. The atomic absorption photospectrometry was utilized for quantifying Na content as the elemental impurity. Prior to the measurement, the solid aliquot was decomposed by a diluted hydrochloric acid. XRF measurement was carried out in order to qualitatively detect the major elemental impurities. TG curve was measured within 1273 K in air flow, for approximately estimating a total amount of the impurity.

2.3. Modification of catalyst

Binary source materials were prepared by blending the powdery scallop shell with basic-MgCO₃ reagent in a mortar, for the purpose of modifying the shell-based catalyst. The basic-MgCO₃/scallop shell blending ratio ranged from 3/7 to 9/1. The prepared binary sources were calcined under the condition mentioned above.

2.4. Rapeseed oil transesterification

Transesterification of rapeseed oil with methanol was carried out with a glass batch reactor system, in order to measure the catalytic activity of CaO deriving from a variety of the source materials. For the employed rapeseed oil, a fatty acid profile was measured on the basis of the JOCS standard method for the analysis of fats, oils and related materials 2.4.1.4-2013 and 2.4.2.3-2013 (Table 1). Primarily, 10 g of the CaO catalyst was stirred into 120 ml of rapeseed oil purchased from a local market in the glass batch reactor, with heating on an electrical hot-plate. The catalyst loading approximated 9 wt% on the basis of a weight of the oil. After a temperature of the catalyst-oil mixture reached 333 K, 60 ml of methanol warmed preliminarily was put in the glass batch reactor for initiating the transesterification. The methanol:oil molar ratio was close to 12. Here, it should be noted that the some experimental batches to collect the crucial data was repeated twice for validating the re-productivity. The error percentage on the basis of the FAME yield was within 3%.

The transesterified product was withdrawn from the glass batch reactor with a glass pipette at the interval of 0.5–1.0 h. The used catalyst was eliminated by the filtration, and then methanol added excessively was removed with a rotary-evaporator. Finally, oil consisting of fatty acids methyl ester (FAME) was collected by decanting the transesterified product in a glass funnel. The collected upper oil phase was analyzed with an Agilent 7890 gas chromatography apparatus, in order to determine yield of FAME on the basis of the EN14103 European biodiesel standard. The gas chromatography apparatus was equipped with a split type injector, a DB-WAX polar capillary column and a flame ionization detector. An error percentage in the measurement of the FAME yield was within 2%.

Table 1
A fatty acid profile of the employed rapeseed oil.^a

Acidity index	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3)
Composition (wt%)	4.2	1.8	62.7	19.3	9.8

^a Based on the JOCS standard method for the analysis of fats, oils and related materials 2.4.1.4-2013 and 2.4.2.3-2013.

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